A potential inversion study of liquid CuBr

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Hard electromagnetic radiation diffraction experiments on copper(I)-bromide melt are presented. Combining the result of this experiment with earlier neutron diffraction experiments the partial pair distribution functions of CuBr have been determined. The differing results for two of these functions obtained recently by various techniques are discussed. A potential inversion scheme has been applied to generate three dimensional structures from the partial pair distribution function. The angular correlations between near neighbor atoms have been determined. These show characteristic differences with the glass-forming $ZnCl_2$ melt. While in $ZnCl_2$ melt the angle joining adjacent $ZnCl_4$ tetrahedra has been found - as in silica glass - well defined and the $+-+$ (ZnClZn) angle distribution peaked the corresponding distribution function in CuBr is broad. This is probably a key to understand, why $ZnCl_2$ but not CuBr melt can be easily supercooled into a glassy state.

61.20.Qg, 61.20.Ja, 61.25 -f

I. INTRODUCTION

Copper-(I)-bromide, like several other copper and silver halides, attains a rather large ionic conductivity before melting, and belongs to a class of ionic systems called fast-ion conductors. A representative of this class of substances, the CuCl, belongs to the first substances investigated by the neutron diffraction with isotopic substitution (NDIS) technique[1]. In this early work, a featureless CuCu partial pair distribution function (PPDF) g_{CuCu} has been found, and this structural detail attracted much attention - including a redetermination and confirmation of the PPDF[2] – as it provides an easy explanation for the fast-ion conductivity: The small copper ions move more or less gas-like through the network of bromine atoms. According to a hypotheses of Ginoza *et al*[3] a structureless cation-cation PPDF should be common to all fast (cat)ion conductors.

The structure of liquid CuBr has been investigated by Allen *et al.*[4] by NDIS making use of the different neutron coherent scattering lengths of $^{65}Cu(6.72 \cdot 10^{-15}$ m) and $^{63}Cu(11.09 \cdot 10^{-15}$ m)[5] to determine the PPDF. Again, a flat, gas-like g_{CuCu} was found in this study. The structure determination by Allen *et al.* has been challenged by DiCicco *et al.*[6], especially concerning the g_{CuBr} PPDF. This group used extended x-ray absorption fine structure (EXAFS) spectroscopy at both the copper and the bromine edge to investigate the short range order in CuBr(l), and found the first shell bromine coordination around copper significantly sharper than determined with neutron diffraction. This is taken by DiCicco *et al.* as an indication that apart from inter-ionic repulsion there is a significant contribution of covalency to the inter-atomic potential. Further, reverse Monte Carlo (RMC) simulations gave evidence[7] that the flat g_{CuCu} is likely to be an artifact of the maximum entropy analysis used in ref. 4.

This paper will address the question about the sharpness of the first CuBr coordination shell. A set of partial structure factors (PSF) is determined consistent with all available diffraction information. Using the potential inversion scheme of Levesque, Weis, Reatto[9] an empirical two body potential is developed. This allows to check the existence of a three-dimensional arrangement of atoms consistent with this set of PSF and to interpret the one-dimensional pair distribution functions in terms of three-dimensional structures. The structure of both CuBr and $ZnCl_2$ melt is characterized by tetrahedral structural units - Zn(II) is isoelectronic with Cu(I). The angular correlation between neighboring atoms is hence discussed comparing these two systems.

II. EXPERIMENTAL

Liquid diffraction experiments have been carried out at the high energy beam-line BW5 at the DORIS-III storage ring at HASYLAB in Hamburg, in the set-up for liquid and amorphous substances[10]. The photon energy was set to 121.0 keV. The covered momentum transfer range was 0.43 Å^{-1} < Q < 26.5 Å^{-1}, with $Q = 4\pi/\lambda \sin(\theta)$, λ is the wave-length and θ half the scattering angle.

The sample (Sigma Chemical Co., quoted purity >99.8%) was sealed under vacuum in a quartz-glass tube of 5 mm inner diameter. The sample was heated to 803 K in a standard neutron diffraction furnace[11]. This furnace – capable

to reach a maximum temperature of 2100K – contains several niobium heat shields the inner most with a radius of 50 mm. As in ref. 12 a restrictive collimation has been used to reduce the background scattering contribution of these niobium shields. Fig. 1 shows the scattering contribution of background and sample. The main contribution to the background is the scattering from the silica container. At low momentum transfers, some powder lines from the niobium shields are remaining in spite of the collimation system. The data points at the positions of these niobium lines are excluded from the further analysis. The usual corrections for detector dead-time, absorption and polarization are made and the intensities are converted into a differential cross section normalizing to the known cross-section (the sum of elastic self scattering and Compton cross section) at large momentum transfers. The data correction procedure is described in more detail in[13].

III. THEORETICAL SUMMARY

The differential cross section of a liquid in a neutron or electromagnetic radiation scattering experiment can be expressed in terms of a total scattering function:

$$S^{(n)}(Q) = \frac{\left(\frac{d\sigma}{d\Omega}\right)^{(n)} - \sum_i^{N_{uc}} \nu_i b_i^2}{(\sum_i^{N_{uc}} \nu_i b_i)^2} + 1 \tag{1}$$

$$S^{(x)}(Q) = i(Q) + 1 = \frac{\left(\frac{d\sigma}{d\Omega}\right)^{(x)}/\sigma_{el} - \sum_i^{N_{uc}} \nu_i f_i^2}{(\sum_i^{N_{uc}} \nu_i f_i)^2} + 1 \tag{2}$$

where $\left(\frac{d\sigma}{d\Omega}\right)$ is the coherent differential cross section, $Q = 4\pi/\lambda \sin(\theta)$, λ the wavelength of the radiation and θ the diffraction angle, b_i the coherent scattering lengths[5], f_i the X-ray form factors in the independent atom approximation[14], σ_{el} the scattering cross section of the free electron, ν_i the stoichiometric coefficient of the atom i, and where the sums are extending over the number of distinct atoms N_{uc} in the unit of composition, CuBr. These total structure functions are composed of partial structure factors s_{ij}:

$$S^{(n/x)} = \sum_{ij} w_{ij}(Q) s_{ij} \tag{3}$$

where

$$w_{ij}(Q) = \frac{\nu_i \nu_j f_i(Q) f_j(Q)}{(\sum \nu_i f_i(Q)^2} \tag{4}$$

and

$$\sum_{ij} w_{ij}(Q) = 1. \tag{5}$$

For the neutron case $f(Q)$ has to be replaced by b and the weighting factors become independent of Q.

The total pair distribution functions are related to the structure factors of Eqs. 1 and 2 via:

$$r \cdot (^{(n/x)}g - 1) = \frac{1}{2\pi^2 \rho_{uc}} \int Q \cdot (^{(n/x)}S(Q) - 1) \sin(Qr) dQ \tag{6}$$

with ρ_{uc} the density per unit of composition. In this work a value of $\rho_{uc} = 0.0175 \, \text{Å}^{-1}$ for CuBr at 800 K has been used to keep consistency with the work of Allen and Howe[4], although an experimental value of $\rho_{uc} = 0.0181 \, \text{Å}^{-1}$ has been reported later by Saito *et al*[15]. Likewise, the partial structure factors are related to the partial pair distribution functions (PPDF) via :

$$r \cdot (g_{ij} - 1) = \frac{1}{2\pi^2 \rho_{uc}} \int Q \cdot (s_{ij} - 1) \sin(Qr) dQ \tag{7}$$

and, hence, the total pair distribution:

$$^{n/x}g(r) = \sum_{ij} \text{FT}[w_{ij}(Q)] \otimes g_{ij} \tag{8}$$

where FT is the Fourier sine transformation and $\otimes$ the convolution operation. The convolution reduces to a simple product in the case of neutron scattering.

An alternative definition of the neutron total structure factor has been used by Allen and Howe[4]:

$$F(Q) = c_a^2 b_a^2 [S_{aa}(Q) - 1] + 2c_a c_b b_a b_b [S_{ab}(Q) - 1] + c_b^2 b_b^2 [S_{bb}(Q) - 1] \tag{9}$$

where c_a, c_b are the concentration of the atomic species, the S_{aa}, S_{bb}, S_{bb} are partial structure factors differing from the s_{ij} in Eq. 3 by a factor of $\sum \nu$. It is noted, that in this definition the total neutron structure factor has the dimension of a cross section, while $S^{(n)}(Q)$ in Eq. 1 is dimensionless.

In order to generate three dimensional structures from the pair distribution functions, the potential inversion scheme of Levesque, Weiss and Reatto[9] (LWR-scheme) has been applied. The idea of this method is based on the equation:

$$g(r) = \exp\left[\frac{-v(r)}{kT} + g(r) - 1 - c(r) + B(r,v)\right] \tag{10}$$

relating the pair distribution function and the pair potential, where $v(r)$ is the pair potential, $c(r)$ the direct correlation function and B(r,v) the bridge function. Starting with a crude guess of the bridge function, e.g. neglecting $B(r,v)$ completely in the hypernetted chain approximation, a first guess of the potential $v^{(1)}$ can be calculated. With a Monte Carlo (MC) or Molecular Dynamics (MD) simulation the pair correlation function $g(r)^{(1)}$ and the direct correlation function $c(r)^{(1)}$ for a system of particles interacting via $v^{(1)}$ can be determined. Thus, the bridge function $B(r, v^{(1)})$ is determined exactly via Eq. 10. $B(r, v^{(1)})$ is assumed to be a better approximation for $B(r, v)$ than the complete neglect in the first approximation. Inserting $B(r, v^{(1)})$ in equation 10 gives the LWR iteration formula:

$$[v^{(n)} - v^{(n-1)}]/kT = \ln(g^{(n-1)}/g^{(exp)})$$
$$+c^{(n-1)} - c^{(exp)} - g^{(n-1)} + g^{(exp)} \tag{11}$$

The empirical potential Monte-Carlo (EPMC) scheme[16] is closely related to equation 11, but considers the upper line of Eq. 11, the logarithmic term only. The complete form of Eq. 11 has been preferred here, as this scheme shows faster convergence[17]. The applicability of the LWR scheme to polyatomic systems has been shown by Kahl $et\ al$[18]. An example of the application of this technique has been given recently in[19].

IV. DEDUCTION OF THE PPDF

In Fig. 2 the total pair distribution function and the total structure factor determined from the hard X-ray experiment are shown. The contribution of g_{CuCu} and g_{BrBr} to $^x g(r)$ $^{(-CuBr,x)}g(r)$ is also shown in Fig. 2. $^{(-CuBr,x)}g(r)$ is calculated according to Eq. 8 as the sum of the PPDF convoluted with $FT(w_{ij}(Q))$. It can be seen, that the first peak in r-space is entirely due to the CuBr-PPDF and, hence, the height of this peak is independent of possible errors in the estimation of the BrBr- and CuCu- PPDF. The corresponding CuBr-PSF is shown in the lower part of Fig. 2. The height of the peak in g_{CuBr} (Fig. 2) is 5.2, clearly higher than than the 3.7 which can be read from Fig. 4 of ref. 4.

Starting point for the determination of the CuCu- and the BrBr-PPDF are the total neutron pair distribution functions[4] for $^{63}CuBr$, $^{63}Cu_{0.5}^{65}Cu_{0.5}Br$ and $^{65}CuBr$. The CuCu- and the BrBr-PPDF used in the preceding paragraph are the result of a direct inversion of the equation system 8. Two additional constraints to the PPDF have been applied, one in Q-space and one in r-space: The CuCu- and BrBr-PPDF show only broad features compared to the CuBr-PPDF, the corresponding PSF oscillate only up to a momentum transfer $Q \sim 10\,\text{Å}^{-1}$ and are set to zero for $Q > 10\,\text{Å}^{-1}$. A minimum allowed distance has been set in r-space to be 2.2 Å for the CuCu-PPDF and 3.1 Å for the BrBr-PPDF. The CuCu- and BrBr-PPDF determined in this way is more structured than the maximum entropy[20] (ME) solution given by Allen $et\ al$[4], as it is to be expected. Using this ME-solution could only reduce the structure in the contribution of these PPDF to the total X-ray pair distribution function in Fig. 2.

Fig. 3 compares the shape of the first CuBr coordination shell determined with EXAFS[6], neutron diffraction[4] and in this work. It is evident, that the ME solution by Allen $et\ al$[4] underestimates the sharpness of the CuBr peak. DiCicco $et\ al$[6], who were the first to deduce a sharper CuBr peak, forwarded the view that this improved result was due to "the exceptional short-range sensitivity" of the EXAFS experiment. It is in fact the result of the use of additional information. Two EXAFS experiments at the bromine and copper edge are in principle incapable to extract three PPDF. Only with the assignment of the first peak in real space to the CuBr-PPDF and the assumption of a Gaussian distribution of the first neighbor shell the problem becomes tractable. This assumption is of course very reasonable

for a system, which melts from a fast ion conductor. Given that, it would be really astonishing, if the like atoms would be the next neighbors in this system.

Introducing the constraints mentioned in the preceding paragraph is largely equivalent to the assumption of next neighborhood of unlike atoms. Thus diffraction gives the information about a sharp CuBr-coordination and, in fact the information about the entire pair distribution function. The very good agreement of the CuBr-PPDF derived form neutron and X-ray diffraction is noted (Fig. 3), if the same constraints are imposed to the analysis of the neutron data. The PPDF determined by the maximum entropy technique are not the real PPDF, nor do they pretend to be the real PPDF. These PPDF have to be interpreted as a lower limit estimation of the structure based on no other information but the neutron diffraction data. They are, in a sense, a prove that the unlike atoms are next neighbors.

Fig. 4 shows a close-up of the first CuBr coordination shell. The peak is strongly asymmetric and clearly cannot be fitted with a single Gaussian distribution. It has been fitted with two Gaussians. The coordination number integrated over both peaks is four.

V. SIMULATION

In order to interpret the PPDF in terms of a three dimensional structure the Levesque, Weis, Reatto potential inversion scheme has been applied to the PPDF shown in Fig. 5. It is evident, that the converged LWR-potentials produce a three dimensional structure in agreement with these PPDF: According to Pusztai and McGreevy[7] the same is not true for the maximum entropy PPDF of Allen and Howe. Contrary to the hypothesis of Ginoza *et al*, that the cation-cation PPDF is structureless in all melts of fast cation conductors, the CuCu PPDF is found similarly structured as the BrBr-PPDF. This finding is in agreement with the RMC study[7]. The agreement of the RMC-PPDF with the PPDF determined here is good for the first CuBr coordination shell and the long distance correlations. Some discrepancies appear at intermediate distances ($\sim 3 - 6$Å). Three facts are certain about the PPDF determined here: They are consistent with all available diffraction information including the new X-ray result. The set of PPDF can be mapped to a three-dimensional arrangement of atoms of the correct density. An effective two-body potential exists with the property, that an ensemble of particles interacting via this potential samples the configuration space consistent with these PPDF.

Some of the angular correlations of near neighbor atoms have been determined from a MC simulation with the converged LWR-potential. These are compared in Fig. 6 to the same functions obtained by RMC[7]. Although there are some differences in the underlying PPDF (cf. Fig. 5), the angular correlations are found to be similar. An interesting detail is perhaps, that the maximum in the Br-Cu-Br distribution function is shifted form $\cos(\angle_{\mathrm{BrCuBr}}) \sim -1/3$ to $\cos(\angle_{\mathrm{BrCuBr}}) \sim 0$, but it is also evident that quoting the maximum of the distribution alone would be misleading.

Fig. 7 compares the angular correlations between neighboring atoms in $ZnCl_2$[21] and CuBr, both obtained using the LWR formalism. Both melts are based on a tetrahedral structural motive and in fact Cu(I) and Zn(II) are isoelectronic species. So some of the distribution functions, the $- + -$ and the $- - -$ distribution function, show similarities. However, there is a pronounced difference in the distribution function of the $+ - +$ angle, the angle joining adjacent tetrahedra. While in $ZnCl_2$ there is a peak at $\cos(\angle_{+-+}) \sim -1./3$. the corresponding angular correlations in CuBr are very weak. As a consequence also the $+ + +$ correlation is much less structured in CuBr than in $ZnCl_2$. Thus a continuous random network is a useful parameterization for the $ZnCl_2$, but not the CuBr structure. The fact, that $ZnCl_2$ but not CuBr can be easily supercooled into a glass is probably intimately related to this difference.

VI. CONCLUSION

The short range order of the melt of the fast-ion conductor Cu(I)Br has been discussed recently. By diffraction experiments with hard electromagnetic radiation it can be conclusively shown, that the first CuBr coordination shell is definitely sharper than obtained earlier in a maximum entropy analysis of NDIS data by Allen *et al*. This is in agreement with the result obtained by DiCicco *et al* using EXAFS spectroscopy. The analysis presented in this work indicates, that the featureless CuCu-PPDF obtained by Allen *et al* is an artifact of the maximum entropy analysis, contrary to the view that a structureless cation-cation PPDF is a common feature in all fast-ion conductors. The same result has been obtained by reverse Monte Carlo by Pusztai *et al*.

The LWR potential inversion scheme has been used to derive an effective two-body potential from the PPDF. This method can be used to interpret the PPDF in terms of a three dimensional structure. A MC simulation with the converged potential has been used to determine angular correlations between near neighbor atoms. The angular correlations in $ZnCl_2$ melt shows similarities in the $- + -$ distribution functions reflecting the similarity in the local environment of the cation. However, while in $ZnCl_2$ the angle between adjacent $ZnCl_4$ tetrahedra is — like in silica

glass — well defined and the $+-+$ angle distribution function is peaked, the corresponding function in CuBr is, as the $+++$ function, broad and featureless. This behavior is probably the key to understand, why $ZnCl_2$ but not CuBr can be easily supercooled into a glassy state.

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FIG. 1. Raw data of the high energy electromagnetic radiation diffraction experiment on CuBr melt at $803\,K$ (scattering contribution from the container, the sample in the container, and the sample scattering after subtraction of the container scattering)

FIG. 2. The total X-ray PDF, the CuBr PPDF and the CuBr-PSF of liquid CuBr.
Upper part of the figure: The total X-ray PDF $^x g(r)$ (shifted -2.0 units in y-direction), the contribution of g_{BrBr} and g_{CuCu} to it (see text) and the resulting CuBr PPDF.
Lower part of the figure: The $Q \cdot (S_{CuBr}(Q) - 1)$ corresponding to the PPDF in the upper part of the figure. The symbols are the experimental points, the solid line is the Fourier back-transform of the PDF in the upper part of the figure, the dashed line is the neutron derived S_{CuBr} (see text). Within the momentum transfer range covered by both experiments the solid and dashed line are almost indistinguishable.

FIG. 3. Comparison of the CuBr-PPDF obtained with various techniques

FIG. 4. Close-up of the first peak in g_{CuCu}. and the Gaussian distributions fitted to it. The midpoints, σ parameter and coordination numbers are given in the figure. The residue is is shown shifted by -0.5 units in y-direction.

FIG. 5. PPDF of CuBr(l).
Comparison of the experimental PPDF (symbols, cf. preceding section), with the PPDF of a MC-simulation with the effective pair-potentials of the LWR-scheme (solid line), the RMC-model i) (dashed dotted line) and ii) (dashed line) from ref.[7]
RMC-model i) and ii) differ significantly only for g_{CuCu} and thus only g_{CuCu} is shown for model i). Model i) and ii) have been obtained by applying the RMC formalism to different scattering functions, either the total structure function of the PPDF.

FIG. 6. Comparison of the angular correlations between adjacent atoms in CuBr(l) determined by RMC-simulation[7] and the LWR-scheme.
Symbols refer to the RMC simulation, the full lines to the LWR scheme using the same cut-off radii as in the RMC work (i.e. Br-Br: 5.2 Å, Cu-Br: 3.3 Å CuCu: 5.2 Å) The dashed lines correspond to a cut-off radius of 3.3 Å (CuCu) and 2.8 Å (CuBr).

FIG. 7. Comparison of the angular correlations between neighboring atoms in CuBr(l) (solid line) and $ZnCl_2$(l) (symbols)[21]